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Published in:
Journal of Physics%3A Condensed Matter

DOI:
[10.1088/0953-8984/11/3/015](https://doi.org/10.1088/0953-8984/11/3/015)

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Document Version
Publisher's PDF, also known as Version of record

Publication date:
1999

[Link to publication in University of Groningen/UMCG research database](#)

Citation for published version (APA):

Ettema, A. R. H. F., & Groot, R. A. D. (1999). Bandstructure calculations of the hexagonal and cubic phases of K3Sb. *Journal of Physics%3A Condensed Matter*, 11(3). <https://doi.org/10.1088/0953-8984/11/3/015>

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Bandstructure calculations of the hexagonal and cubic phases of K_3Sb

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Received 27 July 1998, in final form 15 October 1998

Abstract. The hexagonal and cubic phases of K_3Sb are semiconductors with a band gap of less than 1 eV but optical absorption measurements indicate a band gap which is much larger. This study presents band structure calculations which explain the difference in the band gap values found from conductivity measurements and optical absorption data. Although the experimental values seem to be in conflict, the calculated band structure provides the crucial information to bring the experimental data into agreement.

1. Introduction

The alkali pnictides are an interesting class of compounds with good properties for potential use in thin film applications. The low surface free energies of both constituents are ideal for the growth of flat and smooth films and the band gaps range from ~ 0.1 eV up to 2.5 eV depending on the structure and chemical composition. These compounds appear in two structures: a hexagonal Na_3As structure (space group $P6_3/mmc$) and a face centred cubic structure (space group $Fm\bar{3}m$) [1]. The alkali antimonides have a long history as optically active materials [2, 3].

Most of the alkali pnictides have one stable crystal structure at room temperature, either the hexagonal Na_3As structure or the cubic structure. However K_3Sb appears to be stable in both forms at room temperature. The cubic phase has a brown colour and the hexagonal phase is purple. Upon annealing to higher temperatures cubic K_3Sb makes a transition to the hexagonal phase [3].

Although the alkali antimonides are widely applied because of their good photoemissive and optical properties, the electronic bandstructure has not been studied yet. In this paper we present electronic bandstructure calculations of the cubic and hexagonal phases of K_3Sb and discuss the optical properties.

2. Crystal structures

The hexagonal structure has been determined by Brauer and Zintl [4]. This structure is rather common for the group of alkali pnictides, and called the Na_3As structure [5]. The space group of this structure is $P6_3/mmc$ (No 194), or D_{6h}^4 in Schoenflies notation [6]. The unit cell axes are $a = 6.037$ Å and $c = 10.717$ Å. The antimonide occupies the 2c position with coordinates

$\pm(1/3, 2/3, \bar{1}/4)$, the potassium occupies the 2b position $\pm(0, 0, 1/4)$ and the 4f position $\pm(1/3, 2/3, u; 2/3, 1/3, u+1/2)$ with positional parameter $u = 0.583$. The antimonide atoms have a fivefold coordination in trigonal bipyramids in this structure. The K–Sb distances in the plane of the bipyramid are 3.485 Å and the two K–Sb bonds perpendicular to this plane are 3.572 Å long. A positional parameter for the K atoms at the 4f position of 0.575 would have yield five equal K–Sb distances, therefore the antimony coordination is slightly Jahn–Teller distorted. A hard sphere representation of the trigonal bipyramid is shown in figure 1.

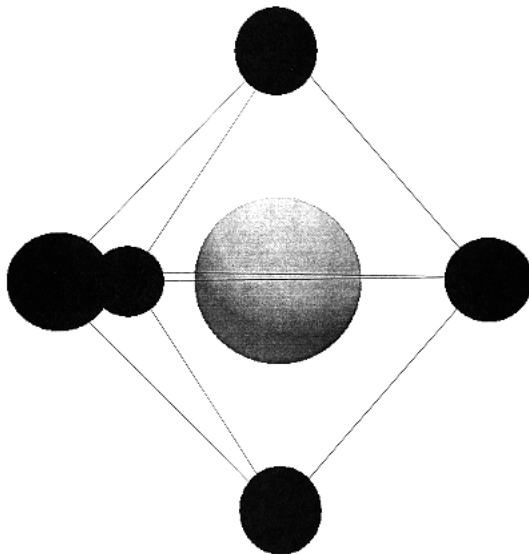


Figure 1. The trigonal bipyramidal coordination of Sb in this structure. The large white spheres represent the potassium atoms and the small black sphere the Sb atom.

The cubic phase has the face centred space group $Fm\bar{3}m$ (No 225), or O_h^4 in Schoenflies notation [3]. The unit cell contains four K_3Sb units ($Z = 4$) and has an axis of length $a = 8.493$ Å. The antimonide atoms occupy the 4a position (0, 0, 0), and the potassium atoms occupy the 4b (1/2, 1/2, 1/2) and the 8c $\pm(1/4, 1/4, 1/4)$ positions. This cubic structure has about 10% denser packing and appears to be more stable for the heavier elements. The antimony atoms have a cubic coordination with the eight potassium atoms at the corners and the antimony atom in the centre. Each antimony atom is surrounded by eight potassium atoms at a distance of 3.678 Å and six potassium atoms at a distance of 4.247 Å. A hard sphere representation of the antimony coordination is shown in figure 2.

3. Bandstructure calculations

The calculations were performed with the localized spherical wave (LSW) method [7]. This method is a modified version of the augmented spherical wave (ASW) method [8]. Exchange and correlation were treated within the local spin density approximation [9]. Scalar relativistic effects were included [10]. In the LSW method the radial parts of the wave functions are described by a numerical solution of the Schrödinger equation within the spheres and augmented by Hankel functions outside the spheres. On neighbouring spheres the Hankel functions are expanded in series of Bessel functions centred on the neighbouring spheres.

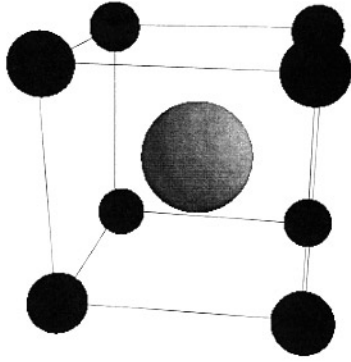


Figure 2. The cubic CsCl coordination of Sb in this structure. The large white spheres represent the potassium atoms and the small black sphere the Sb atom.

Around each atom a cluster is formed with wave functions that fall off rapidly with increasing distance from the central atom.

The basis functions of the K sites were composed of s and p Hankel functions and s, p and d Bessel functions representing the 4s, 4p and 3d states. The basis functions for the antimony atoms were s, p and d Hankel functions and s, p, d and f Bessel functions. The calculations for the hexagonal phase required us to include empty spheres to fill the space in the unit cell. Empty spheres were placed at the 2a position (0, 0, 0) of the corresponding space group. The input parameters of the calculations are shown in tables 1 and 2.

Table 1. Input parameters for the calculation of the hexagonal phase of K_3Sb .

Atom	Position	Start configuration	Sphere radius
K	$2b \pm(0, 0, 1/4)$	$[Ar]4s^1 4p^0(3d^0)$	2.238 Å
K	$4f \pm(1/3, 2/3, 0.583; 2/3, 1/3, 0.083)$	$[Ar]4s^1 4p^0(3d^0)$	2.238 Å
Sb	$2c \pm(1/3, 2/3, 1/4)$	$[Kr]5s^2 5p^3 5d^0$	2.114 Å
Empty sphere	$2a (0, 0, 0; 0, 0, 1/2)$	$1s^0 2p^0$	1.119 Å

Table 2. Input parameters for the calculation of the cubic structure of K_3Sb .

Atom	Position	Start configuration	Sphere radius
K	$8c \pm(1/4, 1/4, 1/4)$	$[Ar]4s^1 4p^0 3d^0$	2.091 Å
K	$4b (1/2, 1/2, 1/2)$	$[Ar]4s^1 4p^0 3d^0$	2.091 Å
Sb	$4a (0, 0, 0)$	$[Kr]5s^2 5p^3 5d^0$	2.091 Å

4. Results

The dispersion of the electron bands calculated for the hexagonal structure is shown in figure 3. The energy, the symmetry and the main orbital character of the bands in the centre (Γ) of the Brillouin zone (BZ) are given in table 3. The bands with an energy higher than 6.2 eV are omitted. The partial and total density of states is given in figure 4.

The lowest bands at -7.4 eV and -7.3 eV are sharp and dominated by the Sb 5s states. The small dispersion of about 0.1 eV indicates that these bands are rather localized.

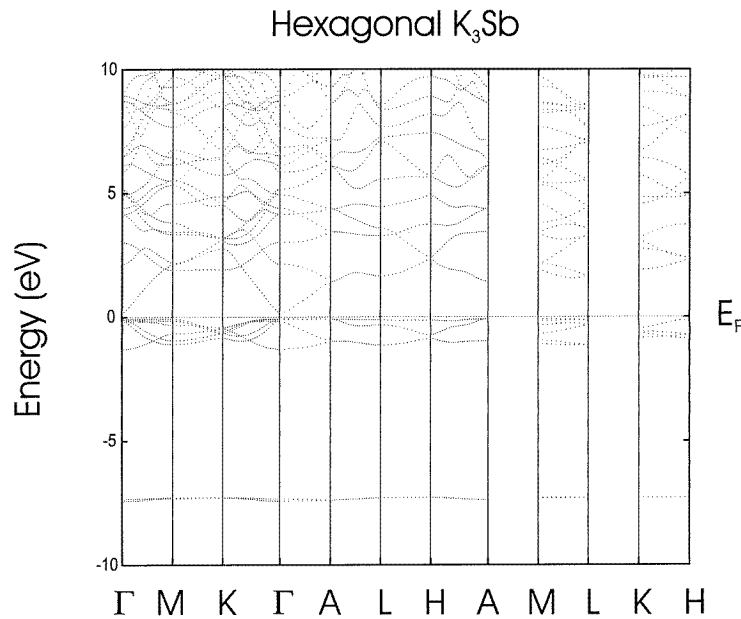


Figure 3. Dispersion of the electron bands along high symmetry lines in the Brillouin zone for the hexagonal structure of K_3Sb . The energy of the bands is given in eV relative to the Fermi level.

Table 3. Energy, symmetry [11] and main orbital character of the electron bands in the centre of the Brillouin zone of the hexagonal structure of K_3Sb .

Energy (eV)	Symmetry	Orbital character
-7.39	Γ_1^+	Sb 5s
-7.31	Γ_4^-	Sb 5s
-1.24	Γ_3^+	Sb 5p _z
-0.14	Γ_2^-	Sb 5p _z
-0.06	Γ_6^+	Sb 5p _{xy}
-0.04	Γ_5^-	Sb 5p _{xy}
0.21	Γ_1^+	K 4s
2.18	Γ_4^-	K 4s
3.06	Γ_3^+	K 4p _z
4.19	Γ_5^-	K 4p _{xy}
4.44	Γ_2^-	K 4p _z
4.98	Γ_6^+	K 4p _{xy}
5.20	Γ_5^+	K 4p _{xy}
5.90	Γ_1^+	K 4s
6.14	Γ_2^-	K 4p _z

The bands between -2 eV and the Fermi level are mainly composed by the Sb 5p orbitals. Although there is some degree of covalency which is also expressed in the partial density of states, the Sb 5p states are the main constituent for the valence band.

The lowest conduction band is a high symmetry band of K 4s states. The density of the conduction band states is appreciable from 1.5 eV to higher energies; between 1.5 eV and 0.2 eV this high symmetry K 4s band has considerable dispersion near the centre of the BZ. Because only one band with much dispersion is present between 0.2 eV and 1.5 eV above the

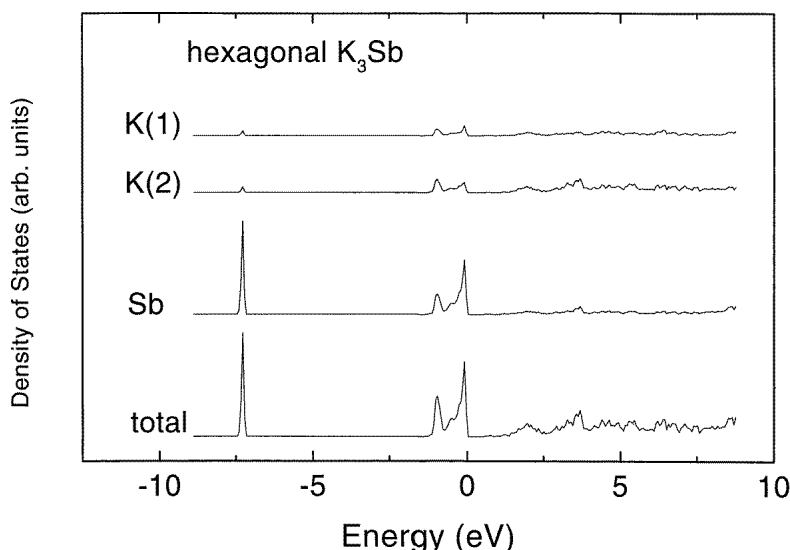


Figure 4. Partial and total density of states distribution of hexagonal K_3Sb . The energy is given in eV relative to the Fermi level.

Fermi level, the density of states is very small in this region. At higher energies bands are present with main orbital character of K 4s, K 4p and Sb 5d.

The optical properties of solids are to a large extent influenced by symmetry. The symmetry of the initial state and the dipole operator determine the symmetry of the final states for a dipole allowed transition. The dipole operator has symmetry representation Γ_5^- for light polarized in the plane of the hexagonal layers. The reduction of the direct product of the Γ_5^- representation with the Sb 5p valence band representations yields irreducible representations of the K 4s and the K 4p_{xy} bands listed in table 3. The K 4p_z bands with the representations Γ_3^+ and Γ_2^- do not have the correct symmetry for a dipole allowed transition from the Sb 5p valence band states. For light polarized perpendicular to the hexagonal plane the symmetry is Γ_2^- and the possible final states for optical transitions from the Sb 5p valence bands have symmetry Γ_1^+ , Γ_4^- , Γ_5^+ or Γ_6^- . In the optical region the accessible conduction bands are dominated by the K 4s states.

The cubic structure has a smaller primitive cell with only one K_3Sb unit and has therefore fewer bands in the first BZ. The dispersions of the electron bands along the high symmetry directions are shown in figure 5. The energy, symmetry and main orbital character is given in table 4. The partial and total density of states are drawn in figure 6.

The lowest valence band has an energy of -7.4 eV below the Fermi level and is also dominated by the Sb 5s states. Again, this state shows hardly any dispersion indicating its localized character.

The valence band just below the Fermi level is threefold degenerate and composed of the Sb 5p states with a small amount of K 4s states. The total width of the valence band is only 1.6 eV. But these bands have considerable dispersion in the X and L direction, which are the bonding directions for the Sb atoms.

The lowest conduction band has an energy of 0.59 eV above the Fermi level at the Γ point in reciprocal space. This band is a high symmetry band made up mainly of K 4s states. Also for this cubic phase the dispersion of this state contributes very modestly to the density of states below an energy of 1.5 eV above the Fermi level.

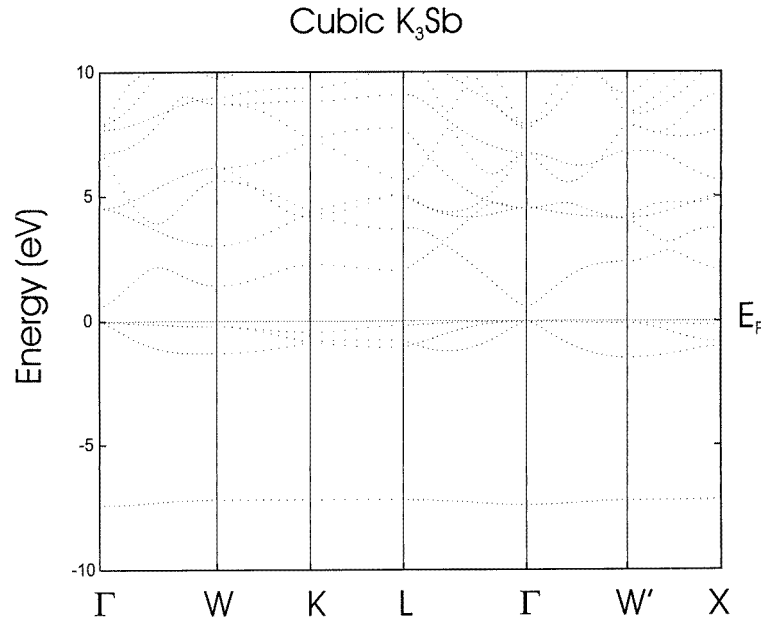


Figure 5. Dispersion of the electron bands along high symmetry lines in the Brillouin zone for the cubic structure of K₃Sb. The energy of the bands is given in eV relative to the Fermi level.

Table 4. Energy, symmetry and main character of the electron bands in the centre of the Brillouin zone of the cubic structure of K₃Sb.

Energy (eV)	Symmetry	Orbital character
-7.40	Γ_1^+	Sb 5s
0.00	Γ_4^-	Sb 5p
0.59	Γ_1^+	K 4s
4.51	Γ_4^-	K 4p
6.74	Γ_4^-	K 4p
7.69	Γ_3^+	Sb 5d (e_g)
7.92	Γ_2^+	K 4s
10.5	Γ_1^+	K 4s
15.1	Γ_5^+	Sb 5d (t_{2g})
15.2	Γ_4^-	K 4p

The second and the third band above the Fermi level are both threefold degenerate and dominated by the K 4p orbitals. The Sb 5d states are split into e_g and t_{2g} levels at Γ with energies of 7.7 eV and 15.1 eV above the Fermi level respectively.

The symmetry of the dipole operator and the Sb 5p valence band states determine the symmetry of possible final states in a dipole transition. The representation of the dipole operator is Γ_4^- and the representation of the initial state is Γ_4^- in the centre of the BZ. The reduction of the direct product of these two representations gives:

$$\Gamma_4^- \otimes \Gamma_4^- = \Gamma_1^+ \otimes \Gamma_3^+ \otimes \Gamma_4^+ \otimes \Gamma_5^+. \quad (1)$$

The final state of a dipole allowed transition is therefore given by the bands that consists of the K 4s and the Sb 5d states.

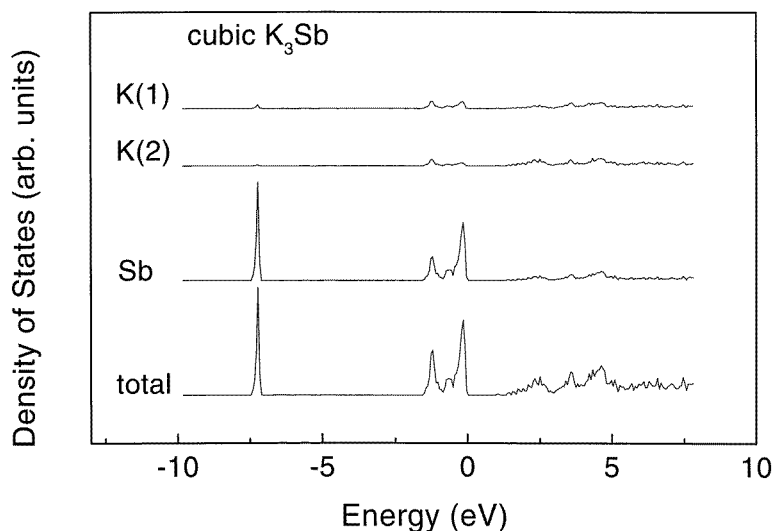


Figure 6. Partial and total density of states distribution of cubic K_3Sb . The energy is given in eV relative to the Fermi level.

5. Discussion and conclusion

The calculated energies of band gaps with atomic sphere approximation methods, like the LSW method, have only a relative meaning because these energies are generally not in accordance with experimental values to high accuracy. An underestimation of the gap is frequently observed in these self-consistent band-structure calculations of semiconductors [12, 13]. Nevertheless, the calculated band gaps for the hexagonal ($E_g = 0.25$ eV) and cubic ($E_g = 0.59$ eV) phase compared with experimental conductivity versus temperature data are in a reasonable agreement. The band gap energies found from conductivity measurements are 0.23 eV and 0.79 eV for the hexagonal and cubic structure respectively [14].

The calculated density of states shows that for the hexagonal phase the absorption starts at photon energies of 0.25 eV with a modest intensity; the absorption is likely to get stronger at higher photon energies of about 1.5 eV. The limited density of the valence band states at an energy of 0.5 eV below the Fermi level between the two peaks can cause a reduced absorption at photon energies of about 2.5 eV. This seems to agree with the observed purple colour of the hexagonal phase and the minimum in the experimental light absorption curves measured by Sommer and McCarroll [3] and Spicer [15]. The estimated band gap values from these optical measurements for the hexagonal and cubic phases are 1.1 eV and 1.4 eV respectively. Although these absorption data [3, 15] seem to be in conflict with the conductivity data [14], from the band structure calculations presented here they are in perfect agreement. The low density of states at the bottom of the conduction band causes only a weak light absorption in the infra-red region of the spectrum.

In conclusion we can state that the calculated band structure explains the discrepancy between the optical absorption data and conductivity measurements. The band gap of both phases is rather small but light absorption is not very strong in the infrared region of the spectrum.

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